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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} **:** C04B 41/00	A2	**(11) International Publication Number:** WO 99/55640 **(43) International Publication Date:** 4 November 1999 (04.11.99)

(21) International Application Number: PCT/US99/09086

(22) International Filing Date: 27 April 1999 (27.04.99)

(30) Priority Data:

60/083,158	27 April 1998 (27.04.98)	US
Not furnished	26 April 1999 (26.04.99)	US

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(81) Designated States: JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

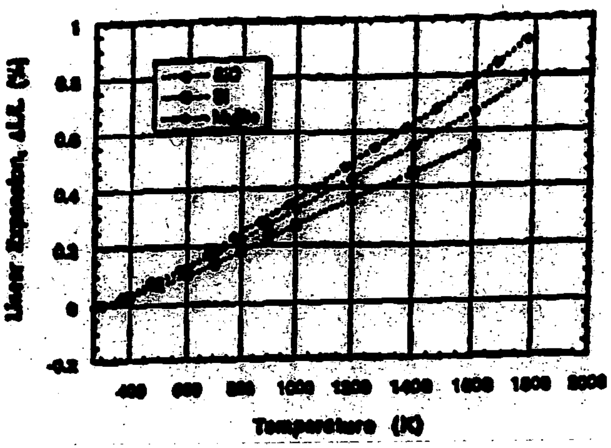
Published

Without international search report and to be republished upon receipt of that report.

(54) Title: COATED ARTICLE AND METHOD OF MAKING

(57) Abstract

An article includes a silicon-containing substrate and a modified mullite coating. The modified mullite coating comprises mullite and a modifier component that reduces cracks in the modified mullite coating. The article can further comprise a thermal barrier coating applied to the modified mullite coating. The modified mullite coating functions as a bond coating between the external environmental/thermal barrier coating and the silicon-containing substrate. In a method of forming an article, a silicon-containing, substrate is formed and a modified mullite coating is applied. The modified mullite coating comprises mullite and a modifier component that reduces cracks in the modified mullite coating.



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COATED ARTICLE AND METHOD OF MAKING

This invention was made with government support under Contract No. NAS3-26385 awarded by NASA. The government may have certain rights in the invention.

BACKGROUND OF THE INVENTION

The invention relates to an article having at least a modified mullite coating. The invention further relates to a silicon-containing substrate having at least a modified mullite coating. The invention further relates to a silicon-containing ceramic substrate having a modified mullite coating and at least one additional layer of material.

Silicon-containing materials have been proposed for structures used in high temperature applications, such as in heat exchangers and advanced internal combustion engines. For example, silicon-based composite ceramics have been proposed as materials for applications in combustors for commercial airplanes. However, these ceramic materials exhibit poor oxidation resistance in reducing atmospheres and in environments containing salts, water vapor or hydrogen. Hence, it is necessary to apply environmental barrier coatings to the silicon-containing materials to provide protection from environmental attack at elevated temperatures and to apply thermal barrier coatings to extend the life at elevated temperatures.

Mullite has been proposed as a material for environmental barrier coatings as well as thermal barrier coatings on silicon-containing materials. Mullite exhibits low thermal conductivity. It has low density and a high melting point. However, mullite coatings tend to develop cracks perpendicular to substrates and through the thickness of the coating. These cracks are detrimental to the functions of the mullite coating because they serve as transport paths for corrosive species causing severe oxidation and corrosion at the interface between the coating and substrate. Additionally, cracks in the coating concentrate stresses. The cracks apply shear and tensile forces on the substrate to cause substrate fractures.

Since the crack openings increase with increasing distance from the mullite substrate interface, the cracks may be the result of the difference in thermal expansion between the mullite coating and the silicon-containing substrate. FIG. 1 shows differences in the coefficient of thermal expansion (CTE) of mullite, silicon carbide (SiC) and silicon (Si). Thus, there is a need to provide coatings or layers to silicon-containing substrates that act at least as environmental barrier coatings having reduced cracks.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that a modifier component can be added to a mullite coating to reduce cracks in the coating applied to a silicon-containing substrate. The mullite coating with the modifier component is also referred to as a modified mullite coating. The modified mullite coating reduces fracture at the interface of the mullite coating and the silicon-containing substrate.

In one aspect, the invention is an article comprising a silicon-containing substrate and a modified mullite coating. The modified mullite coating comprises mullite and a modifier component that reduces cracks, including through-thickness cracks, in the mullite coating. Preferably, the modifier component comprises a component having a lower thermal expansion than the mullite coating. As a result, the modifier component imparts a lower thermal expansion coefficient to the mullite coating. The article can further comprise an external environmental/thermal barrier coating applied to the modified mullite coating. The modified mullite coating then functions as a bond coat between the external environmental/thermal barrier coating and the silicon-containing substrate.

In another aspect, the invention relates to a method of forming an article with at least a modified mullite coating. In the method, a silicon-containing substrate is formed and a modified mullite coating is applied. The modified mullite coating comprises mullite and a modifier component that reduces cracks in the coating.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph illustrating comparative coefficient of thermal expansions for mullite, silicon carbide and silicon.

FIG. 2 is a graph illustrating comparative coefficient of thermal expansions for mullite, cordierite, fused silica and celsian ($BaO \bullet Al_2O_3 \bullet 2SiO_2$).

FIG. 3 is a photomicrograph for a mullite and yttria stabilized zirconia-coated silicon carbide/silicon carbide composite.

FIG. 4 is a photomicrograph for a mullite with twenty-two volume percent calcium aluminosilicate and a yttria stabilized zirconia-coated silicon carbide/silicon carbide composite; and

FIG. 5 is a photomicrograph for a mullite with eighteen volume percent barium strontium aluminosilicate and a yttria stabilized zirconia-coated silicon carbide/silicon carbide composite.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention, a modifier component is added to a mullite coating to reduce or eliminate cracks, including through-thickness cracks. By through thickness-cracks is meant cracks that extend substantially through the entire thickness of the mullite coating from near the top surface to near the bottom of the coating or near the silicon-containing substrate. The modifier components can be categorized into one or more of at least three functional groups. (1) The modifier component imparts a closer coefficient of thermal expansion (CTE) match between the modified mullite coating and silicon-containing substrate than the coefficient of thermal expansion match between the mullite coating without the modifier and the silicon-containing substrate. (2) The modifier component provides a phase or phases that reduce the overall elastic modulus of the modified mullite coating to reduce thermal stress in said coating. (3) The modifier component provides a phase or phases that serve as crack arresters to increase resistance of the modified mullite coating to crack propagation. The modifer component increases the toughness of the modified mullite coating.

The modified mullite coating is applied to a silicon-containing substrate. Suitable silicon-containing substrates comprise materials that result in cracking of an applied mullite coating. The silicon-containing substrate can comprise a ceramic such as a silicon-based ceramic. Examples are silicon carbide, silicon nitride, silicon carbon nitride, silicon oxynitride, and the like. The silicon- containing ceramic substrate can be a monolith or composite. A composite can comprise a silicon, silicon carbide, carbon or mixtures thereof reinforcing fibers, particulate or whiskers and a silicon-based matrix. The fibers. particulate and whiskers generally have at least one outer coating, such as silicon carbide, silicon boride, silicon nitride and the like. The matrix can be processed by melt infiltration (MI), chemical vapor infiltration (CVI) or other technique. Exemplary silicon-containing substrates include a monolithic silicon carbide and silicon nitride substrate, a silicon carbide fiber-reinforced silicon carbide matrix composite, carbon fiber-reinforced silicon carbide matrix composite, and a silicon carbide fiber-reinforced silicon nitride composite. The preferred substrate comprises a silicon carbide fiber-reinforced silicon-silicon carbide matrix composite processed by silicon melt infiltration.

Also suitable as silicon-containing substrates are silicon metal alloys. These alloys include niobium silicon alloys, molybdenum silicon alloys and the like.

The coated article of the invention can comprise a thermal barrier coating applied to the modified mullite coating. Suitable external environmental/thermal barrier coatings include chemically stabilized zirconias, such as yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia and magnesia-stabilized zirconia, alumina and alumina silicate. Preferred external environmental/thermal barrier coatings in this invention include yttria-stabilized zirconia (YSZ), barium strontium aluminosilicate (BSAS), calcium aluminosilicate (CAS) and yttrium silicates (YS).

The modified mullite coating of the invention comprises mullite and a modifier component that reduces cracks in the modified mullite coating. Mullite is a stable form of aluminum silicate found naturally or formed by heating other aluminum silicates such as cyanite, sillimanite and andalusite, to high temperature. Mullite is an excellent high temperature material (incongruent melting temperature about 1830C) with high corrosion resistance, high thermal shock resistance and chemical stability at high temperatures, such as up to about 1700C. It is the only stable crystalline compound in the aluminum silicate system under normal atmospheric pressure. It has a chemical composition ranging from $3Al_2O_3{\cdot}2SiO_2$ (71.8 wt% Al_2O_3) (3/2 mullite) to approximately $2Al_2O_3{\cdot}SiO_2)_2$ (77.3 wt%Al_2O_3)(2/1 mullite). It crystallizes in the orthorhombic system. It has a melting point of 1850 C. and a coefficient of thermal expansiion of 5.62×10^{-6}/ C in the 25-1500 C range. In the absence of glassy inclusions, mullite retains greater than 90%

of its room temperature strength to 1500 C and displays very high creep and thermal shock resistance.

Examples of suitable modifier components of the modified mullite coating include alkaline earth aluminosilicates, preferably with the formula $MO\bullet Al_2O_3\bullet 2SiO_2$, where M is an alkaline earth element. Preferred modifier components of the formula $MO\bullet Al_2O_3\bullet 2SiO_2$ include barium feldspar ($BaO\bullet Al_2O_3\bullet 2SiO_2$), strontium feldspar ($SrO\bullet Al_2O_3\bullet 2SiO_2$), and combinations of barium feldspar ($BaO\bullet Al_2O_3\bullet 2SiO_2$), and strontium feldspar ($SrO\bullet Al_2O_3\bullet 2SiO_2$). Preferably, the alkaline earth aluminosilicate has a monoclinic celsian crystalline phase. Most preferred aluminosilicates include $(BaO)_{0.75}(SrO)_{0.25}\bullet Al_2O_3\bullet 2SiO_2$ referred to as BSAS, $CaO\bullet Al_2O_3\bullet 2SiO_2$ referred to as CAS and $BaO\bullet Al_2O_3\bullet 2SiO_2$. Other suitable modifiers include materials referred to as NZP's such as $NaZr_2P_3O_{12}$, $Ba_{1.25}Zr_4P_{5.5}Si_{0.5}O_{24}$, $Ca_{0.5}Sr_{0.5}Zr_4(PO_4)_6$ and $Ca_{0.6}Mg_{0.4}Sr_4\ (PO_4)_6$. Other preferred modifier components include yttrium silicates, calcium aluminates including $3Ca_{0.5}\bullet 5\ Al_2O_3$, aluminum titanates including $Al_2O_3\bullet TiO_3$, cordierite ($2MgO\bullet Al_2O_3\bullet 5\ SiO_2$), fused silica ($SiO_2$) and silicon (Si). These materials are also chemically compatible with mullite.

The modifier components may be added to the modified mullite coating in a percent volume range between about 5 to about 50. Preferably, the modifier component is present in about 10 to about 30 volume percent of the modified mullite coating and most preferably in about 15 to 25 volume percent.

In the group (1) modifier components, a coefficient of thermal expansion is imparted to the modified mullite coating that is closer to the coefficient of thermal expansion of the silicon-containing substrate. The coefficient of thermal expansion of a polycrystalline composite material is determined by the volume fractions of its constituents. The coefficient of thermal expansion can generally be approximated by using the rule of mixture:

$$\underline{\alpha}_c = \underline{\alpha}_1 V_1 + \underline{\alpha}_2 V_2 + \ldots \underline{\alpha}_i V_i$$

where $\underline{\alpha}_c$ is the coefficient of thermal expansion of the composite, and $\underline{\alpha}_1, \underline{\alpha}_2$ and $\underline{\alpha}_i$ and V_1, V_2 and V_i are the coefficient of thermal expansions and volume fractions of phases 1, 2 and i, respectively. Therefore, adding a phase or phases with lower coefficient of thermal expansion to a material will result in a composition that has a lower coefficient of thermal expansion than the starting material. To duplicate the coefficient of thermal expansion of the silicon-containing substrate, the volume faction of the modifier component in the modified mullite coating should be proportionate to the ratio of the difference between the coefficient of thermal expansion of the silicon-containing substrate and the coefficient of thermal expansion of the mullite to the difference between the coefficient of thermal expansion of the modifier component and the coefficient of thermal expansion of the mullite.

A comparison of coefficient of thermal expansion of mullite with the coefficient of thermal expansions of cordierite, fused silica and celsian ($BaO \bullet Al_2O_3 \bullet 2SiO_2$) is illustrated in Fig. 2. According to the invention, co-depositing mullite with a low thermal expansion modifier component such as cordierite, fused silica or celsian ($BaO \bullet Al_2O_3 \bullet 2SiO_2$) on silicon or silicon-containing ceramic substrates or ceramic composite substrates imparts an improved thermal expansion match of the modified mullite coating with the silicon-containing substrate than with a monolithic mullite coating.

Cordierite is an incongruently melting compound with mullite formed first when cooling from the liquid phase. Upon quenching form the melt splash during the plasma spray, it may remain as a glassy material or mullite with a glass phase. This may require a post-spray annealing process at appropriate temperatures to convert the material to cordierite. The amount of modifier component addition can be first estimated by the rule of mixture estimate. But because of the complexity of phase composition in the system, a trial and error process may have to be executed before an optimal proportion is reached.

The mullite coating with the modifier component can be applied to the silicon-containing substrate by any suitable method including thermal spray, air plasma spray (APS) and vacuum or low pressure plasma spray (VPS or LPPS), high velocity oxy-fuel (HVOF) spray, vapor deposition, including chemical vapor deposition (CVD), physical vapor deposition (PVD) and solution techniques such as sol-gel, slurry coating or colloidal suspension coating. A constituent starting powder of the mullite coating and modifier component may be premixed through a vigorous mechanical process, such as ball milling, to provide interlocking of the powders and prevent segregation of phases due to density differences. For the same purpose, a sol-gel or colloidal process may be employed to coat the particles of one constituent with another.

Sarin *et al.*, U.S. Pat. 5,763,008 and Lee *et al.*, U.S. Pat. 5,496,644 describe exemplary methods of applying mullite coatings. The disclosures of these patents are incorporated herein by reference. Sarin *et al* discloses a chemical deposition process comprising steps of establishing a flow of reactants which will yield mullite in a CVD reactor, and depositing a crystalline coating from the reactant flow. Lee *et* al. discloses a method of plasma spraying mullite coatings onto silicon-based ceramic materials. The method prevents deposition of amorphous mullite by heating the silicon-containing substrate to a very high temperature (greater than 1000C) during the spraying process.

The following examples are illustrative of the invention.

Examples

Powders of $CaO \bullet Al_2O_3 \bullet 2SiO_2$ (CAS) (22 vol%) and $(BaO)_{0.75}(SrO)_{0.25} \bullet Al_2O_3 \bullet 2SiO_2$ (BSAS) (18 vol%) were added to mullite powder by ball milling, respectively. The composite powders were sprayed using air plasma spray (APS) onto a silicon carbon fiber reinforced silicon carbide-silicon matrix composite substrate processed by melt infiltration. The substrate temperature was kept at 1050 to 1250 C. The plasma torch model was Electro-plasma 03CA, with 45 kW power, argon (14.4 SLM) as primary gas and helium (9.8 SLM) as secondary gas. Plasma torch to substrate distance was 4". A top coat of yttria-stabilized zirconia (YSZ) was applied on top of the composite mullite coating by air plasma spray using standard operating procedures for thermal barrier coatings. A baseline sample of monolithic mullite coating on the ceramic composite substrate was also prepared using the thermal spray technique with a yttria-stabilized zirconia topcoat.

Samples of silicon-containing ceramic substrates with the modified mullite and thermal barrier coatings and monolithic mullite coatings were subjected to an environmental furnace test with two hour cycles from room temperature to 1300 C for 500 hours in 90%H_2O 10%O_2. The results are shown in Figs 3-5.

Figure 3 shows that through-thickness cracks developed in the baseline sample with the monolithic mullite coating. Extensive oxidation of the silicon-based ceramic composite at the mullite/substrate interface resulted in failure of the mullite coating (environmental barrier coating) during the test.

In contrast, the composite modified mullite coatings shown in Figs. 4 and 5 exhibited no through-thickness cracks in the modified mullite coating and the coatings survived the test with minimal change at the modified mullite coating/substrate interface.

WHAT IS CLAIMED:

1. An article comprising:

a silicon-containing substrate; and

a modified mullite coating comprising mullite and a modifier component that reduces cracks in the modified mullite coating.

2. The article of claim 1, wherein said modifier component comprises a lower thermal expansion component than mullite that imparts a closer coefficient of thermal expansion match between said modified mullite coating and said silicon-containing substrate.

3. The article of claim 1, wherein said modifier component forms a phase in said modified mullite coating that reduces thermal stress in the modified mullite coating by reducing the elastic modulus of said modified mullite coating.

4. The article of claim 1, wherein said modifier component forms a phase in said modified mullite coating that arrests the propagation of cracks in said modified mullite coating.

5. The article of claim 1, wherein said modifier component comprises an alkaline earth aluminosilicate.

6. The article of claim 1, wherein said modifier component comprises a modifier component of the formula $MO \bullet Al_2O_3 \bullet xSiO_2$, where M is an alkaline earth element and $1 \leq x \leq 3$.

7. The article of claim 1, wherein said modifier component comprises barium feldspar ($BaO \bullet Al_2O_3 \bullet 2SiO_2$), strontium feldspar ($SrO \bullet Al_2O_3 \bullet 2SiO_2$) or a combination of barium feldspar ($BaO \bullet Al_2O_3 \bullet 2SiO_2$),

and strontium feldspar ($SrO \bullet Al_2O_3 \bullet 2SiO_2$).

8. The article of claim 1, wherein said modifier component comprises a monoclinic celsian crystalline phase.

9. The article of claim 1, wherein said modifier component comprises barium strontium aluminosilicate (BSAS), calcium aluminosilicate (CAS), yttrium silicate (YS) or a combination thereof.

10. The article of claim 1, wherein said modifier component comprises an NZP (NaZr2P3O12) modifier.

11. The article of claim 10, wherein said modifier component comprises $NaZr_2P_3O_{12}$, $Ba_{1.25}Zr_4P_{5.5}Si_{0.5}O_{24}$, $Ca_{0.5}Sr_{0.5}Zr_4(PO_4)_6$ or $Ca_{0.6}Mg_{0.4}Sr_4(PO_4)_6$.

12. The article of claim 1, wherein said modifier component comprises a calcium aluminate or an aluminum titanate.

13. The article of claim 1, wherein said modifier component comprises 3Ca0.5•5 Al2O3, or Al2O3•TiO2.

14. The article of claim 1, wherein said modifier component comprises cordierite (2MgO•2Al2O3•5SiO2), fused silica (SiO2) silicon (Si), or mixture thereof.

15. The article of claim 1, wherein said silicon-containing substrate is a monolithic or composite silicon carbide/silicon ceramic.

16. The article of claim 1, wherein said silicon-containing substrate is a monolithic or composite silicon nitride.

17. The article of claim 1, further comprising an external environmental/thermal barrier coating applied to said modified mullite coating.

18. The article of claim 17, wherein said modified mullite coating functions as a bond coating between said external environmental/thermal barrier coating and said silicon-containing substrate.

19. The article of claim 17, wherein said thermal barrier coating comprises yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, magnesia-stabilized zirconia, alumina or alumina silicate.

20. The article of claim 2, wherein a volume faction of the modifier component in the modified mullite coating is proportionate to a ratio of a difference between a coefficient of thermal expansion of the silicon-containing substrate and the coefficient of thermal expansion of a mullite to a difference between a coefficient of thermal expansion of the modifier component and the coefficient of thermal expansion of the mullite.

21. A method of forming an article, comprising; forming a silicon-containing substrate; and applying a modified mullite coating comprising mullite and a modifier component that reduces cracks in the modified mullite coating.

22. The method of claim 21, further comprising annealing said modified mullite coating to convert a glass phase of said modifier component to a phase compatible with said mullite.

23. The method of claim 21, further comprising applying an external environmental/thermal barrier coating onto said modified mullite coating.

24. The method of claim 21, wherein said modifier component comprises a lower thermal expansion component than mullite that imparts a closer coefficient of thermal expansion match between said modified mullite coating and said silicon-containing substrate.

25. The method of claim 21, wherein said modifier component forms a phase in said modified mullite coating that reduces thermal stress in the modified mullite coating by reducing the elastic modulus of said modified mullite coating.

26. The method of claim 21, wherein said modifier component forms a phase in said modified mullite coating that arrests the propagation of cracks in said modified mullite coating.

27. The method of claim 21, wherein said modifier component comprises alkaline earth aluminosilicates.

28. The method of claim 21, wherein said modifier component comprises a modifier component of the formula MO•AL2O3•2SiO2, where M is an alkaline earth element.

29. The method of claim 21, wherein said modifier component comprises barium feldspar (BaO•Al2O3•2SiO2), strontium feldspar (SrO•Al2O3•2SiO2) or a combination of barium feldspar (BaO•Al2O3•2SiO2), and strontium feldspar (SrO•Al2O3•2SiO2).

30. The method of claim 21, wherein said modifier component comprises a monoclinic celsian crystalline phase.

31. The method of claim 21, wherein said modifier component comprises barium strontium aluminosilicate (BSAS), calcium aluminosilicate (CAS), yttrium silicate (YS) or a combination thereof.

32. The method of claim 21, wherein said modifier component comprises an NZP modifier.

33. The method of claim 32, wherein said modifier component comprises NaZr2P3O12, Ba1.25Zr4P5.5Si0.5O24, Ca0.5Sr0.5Zr4(PO4)6 or Ca0.6Mg0.4Sr4 (PO4)6.

34. The method of claim 21, wherein said modifier component comprises a calcium aluminate or an aluminum titanate.

35. The method of claim 21, wherein said modifier component comprises 3Ca0.5•5 Al2O3, or Al2O3•TiO3.

36. The method of claim 21, wherein said modifier component comprises cordierite (2MgO•2Al2O3•5SiO2), fused silica (SiO2) or silicon (Si).

37. The method of claim 21, comprising adding a volume faction of the modifier component in the modified mullite coating is proportionate to a ratio of a difference between a coefficient of thermal expansion of the silicon-containing substrate and the coefficient of thermal expansion of a mullite to a difference between a coefficient of thermal expansion of the modifier component and the coefficient of thermal expansion of the mullite.

38. The method of claim 21, comprising applying said modified mullite coating by thermal spray, high velocity oxy-fuel (HVOF) spray, vapor deposition, physical vapor deposition (PVD) or solution technique.

39. The method of claim 21, comprising applying said modified mullite coating by air plasma spray, vacuum plasma spray or low pressure plasma spray.

40. The method of claim 21, comprising applying said modified mullite coating by chemical vapor deposition.

41. The method of claim 21, comprising applying said modified mullite coating by sol-gel, slurry coating or colloidal suspension coating.

42. The method of claim 21, comprising forming the modified mullite coating by first forming a starting powder of the coating and modifier component by ball milling.

43. The method of claim 21, comprising forming the modified mullite coating by a sol-gel or colloidal process.

44. A method for making a coated article comprising forming a silicon/silicon carbide composite having silicon carbide-containing fibers; applying a modified mullite coating comprising mullite and barium strontium aluminosilicate (BSAS), that reduces cracks in the modified mullite coating; and optionally applying a yttria-stabilized zirconia coating to the modified mullite coating.

45. A coated article comprising a silicon/silicon carbide composite having silicon carbide-containing fibers; a modified mullite coating comprising mullite and barium strontium aluminosilicate (BSAS), that reduces cracks in the modified mullite coating; and optionally a yttria-stabilized zirconia coating on the modified mullite coating.

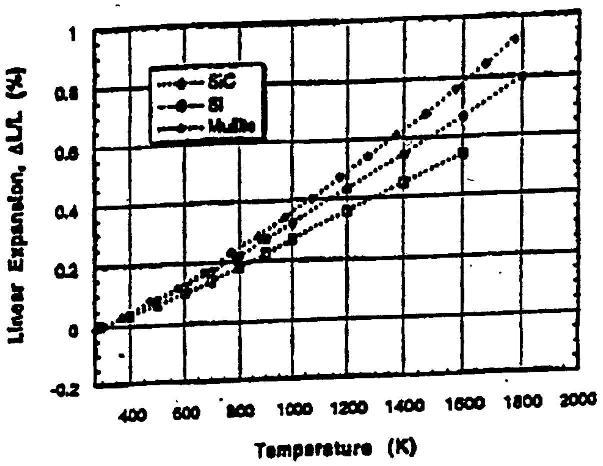
SiC
Si
MoSi2
Linear Expansion, ΔL/L (%)
1
0.8
0.6
0.4
0.2
0
-0.2
400
600
800
1000
1200
1400
1600
1800
2000
Temperature (K)

Fig.1.

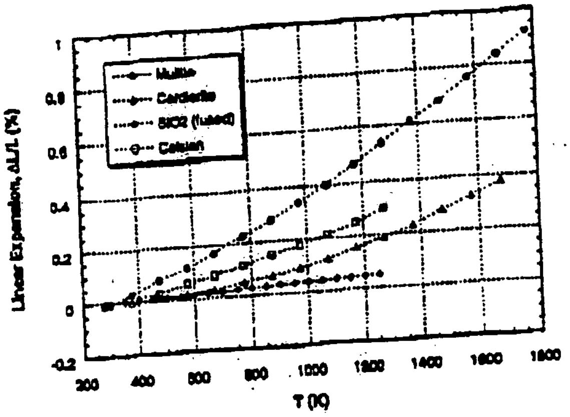
Mullite
Cordierite
SiO2 (fused)
Celsian
Linear Expansion, ΔL/L (%)
1
0.8
0.6
0.4
0.2
0
-0.2
200
400
600
800
1000
1200
1400
1600
1800
T (K)

FIG. 2

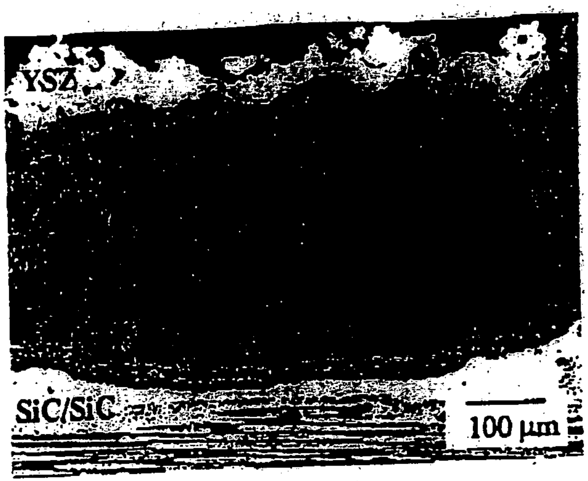

FIG. 3

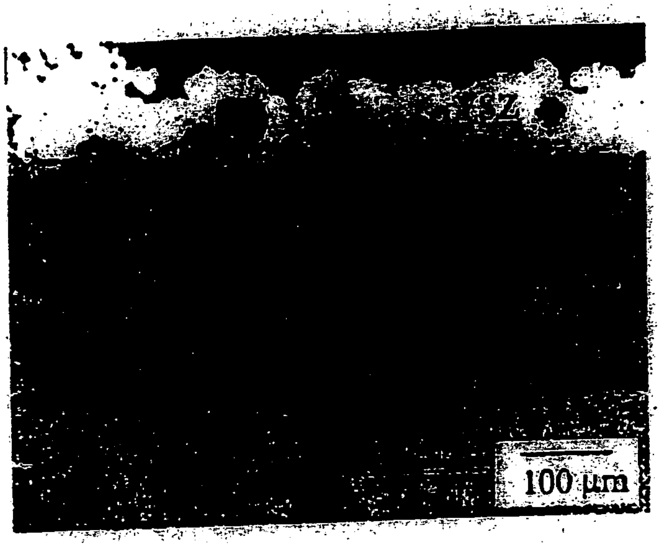

FIG. 4

FIG. 5

CORRECTED VERSION*

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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} :
C04B 41/87

A3

(11) International Publication Number: WO 99/55640

(43) International Publication Date: 4 November 1999 (04.11.99)

(21) International Application Number: PCT/US99/09086

(22) International Filing Date: 27 April 1999 (27.04.99)

(30) Priority Data:

60/083,158	27 April 1998 (27.04.98)	US
Not furnished	26 April 1999 (26.04.99)	US

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(81) Designated States: JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(88) Date of publication of the international search report:
20 January 2000 (20.01.00)

(54) Title: ARTICLE HAVING A MODIFIED MULLITE COATING AND METHOD OF MAKING THE SAME

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INTERNATIONAL SEARCH REPORT

International Application No
PC./US 99/09086

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B41/87

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 20903 A (UNIV BOSTON) 11 July 1996 (1996-07-11) page 10, line 16 -page 11, line 16; figure 3 ---	1,17,21, 40
X	US 4 839 316 A (TIEGS TERRY N) 13 June 1989 (1989-06-13) column 2, line 63 -column 4, line 46; figures 1,2 ---	1,15,17, 21,41
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 032 (C-1154), 18 January 1994 (1994-01-18) & JP 05 262585 A (TOSHIBA CORP), 12 October 1993 (1993-10-12) abstract --- -/--	1,17,21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 3 November 1999	Date of mailing of the international search report 12/11/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rauscher, M

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/09086

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 332 619 A (LACOSTE MARC ET AL) 26 July 1994 (1994-07-26) column 4, line 34 - line 58 -----	1,17,23, 39

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Information on patent family members

International Application No
PCT/US 99/09086

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU 4963496 A	24-07-1996
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		DE 69229513 D	12-08-1999
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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 November 1999 (04.11.1999)

PCT

(10) International Publication Number
WO 99/55640 A3

(51) International Patent Classification⁶: C04B 41/87

(21) International Application Number: PCT/US99/09086

(22) International Filing Date: 27 April 1999 (27.04.1999)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/083,158 27 April 1998 (27.04.1998) US
09/299,419 26 April 1999 (26.04.1999) US

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Published:
— *With international search report.*

(88) Date of publication of the international search report: 20 January 2000

(48) Date of publication of this corrected version: 15 March 2001

(15) Information about Corrections:
see PCT Gazette No. 11/2001 of 15 March 2001, Section II
Previous Corrections:
see PCT Gazette No. 09/2000 of 2 March 2000, Section II
see PCT Gazette No. 50/1999 of 16 December 1999, Section II

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